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(54) Title: PROCESS FOR THE PREPARATION OF DISULFIDES FROM THIOLS

(57) Abstract

The process oxidizes thiols to disulfides using elemental selenium as a catalyst. Elemental selenium complexes with the thiol to form the species $RSSe^-$ which is rapidly oxidized by molecular oxygen to the disulfide RSSR.

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Description

Process for the preparation of disulfides from thiols

The present invention relates to a process for the preparation of disulfides by oxidizing thiols in the presence of a catalyst in aqueous solution.

Several catalysts are known to catalyze the oxidation of thiols to disulfides according to the equation

$$2\,RSH + \tfrac{1}{2}O_2 \longrightarrow RSSR + H_2O \qquad (1)$$

These catalysts include $CuCl_2$, $FeCl_3$, and Na_2SeO_3. The preparation of disulfides as a result of the oxidation of alkylthiols with O_2 in the presence of cuprous chloride has been described in an article by D.W. Giles, J.A. Cha and P.K. Lim in Chemical Engineering Science, Vol.41, No.12, pp.3129-3140, 1986.

The present invention provides a process for the preparation of disulfides in aqueous solution by oxidizing thiols with molecular oxygen in the presence of a catalyst in the temperature range in which water is a liquid.

$$2\,RSH + \tfrac{1}{2}O_2 \xrightarrow{Se^{\circ}} RSSR + H_2O \qquad (2)$$

(R = H, alkyl group or other organic moieties)

The catalyst is elemental selenium which is solubilized by complexing with sulfides according to the equation

$$RS^- + Se \rightleftharpoons RSSe^- \qquad (3)$$

The thiol containing molecule that was used is mercaptoethanol which was deprotonated using sodium hydroxide solution

$$HOCH_2CH_2SH + NaOH \longrightarrow HOCH_2CH_2S^-Na^+ + H_2O \qquad (4)$$

The deprotonated mercaptoethanol complexes with selenium according to the equilibrium

$$HOCH_2CH_2S^- + Se \rightleftharpoons HOCH_2CH_2SSe^- \qquad (5)$$

The equilibrium constant for the above equilibrium is given by the equation

$$K = \frac{[HOCH_2CH_2SSe^-]}{[HOCH_2CH_2S^-]} \qquad (6)$$

The equilibrium constant was found to be 0.36. Saturation was achieved after approximately 2 hours of vigorous stirring. If oxygen is passed through the solution containing $HOCH_2CH_2SSe^-$ anions, the $HOCH_2CH_2SSe^-$ anions are rapidly oxidized to the disulfide $HOCH_2CH_2SSCH_2CH_2OH$ with a yield exceeding 95%. Selenium catalyzes the oxidation of thiols according to the equations

$$\begin{matrix} (\ RS^- + Se \rightleftharpoons RSSe^-\ ) \\ 2RS^- + 2H^+ + \tfrac{1}{2}O_2 \longrightarrow RSSR + H_2O \end{matrix} \qquad (7)$$

As the $HOCH_2CH_2SSe^-$ anions are oxidized, the solubilized selenium precipitates out of solution in the form of grey selenium. Eventually, all the solubilized selenium precipitates out of solution.

Example

0.5g of selenium and 50ml of water was placed in a 250ml flask. 0.5ml of mercaptoethanol was added to the flask. The mercaptoethanol was deprotonated by adding 71.68ml of 0.1N NaOH to the flask. The solution was stirred with a magnetic stirring bar until equilibrium was reached after 2 hours. Oxygen was passed through the solution for 10 minutes using a fritted glass attachment to oxidize mercaptoethanol to the disulfide $HOCH_2CH_2SSCH_2CH_2OH$.

THE EMBODIMENT OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED IS DEFINED AS FOLLOWS:

1. A process for preparing disulfides in aqueous solution by oxidizing thiols with oxygen in the presence of a catalyst characterized in that the catalyst is elemental selenium.

2. A process according to claim 1 in which the thiols have the formula R-SH wherein R is hydrogen, an alkyl group or other organic moieties.

3. A process according to claim 1 or 2 in which sodium hydroxide is added.

AMENDED CLAIMS

[received by the International Bureau on 26 November 1993 (26.11.93); original claim 2 amended; other claims unchanged (1 page)]

THE EMBODIMENT OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED IS DEFINED AS FOLLOWS:

1. A process for preparing disulfides in aqueous solution by oxidizing thiols with oxygen in the presence of a catalyst characterized in that the catalyst is elemental selenium.

2. A process according to claim 1 in which the thiols have the formula R-SH wherein R is hydrogen or alkyl.

3. A process according to claim 1 or 2 in which sodium hydroxide is added.

INTERNATIONAL SEARCH REPORT

International Application No PCT/CA 93/00055

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07C319/24; C07C323/12

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[9]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	CHEMICAL AND ENGINEERING SCIENCE, vol. 41, no. 12, 1986, Oxford, GB, pages 3129 - 3140 D.W. GILES, ET AL.: 'The aerobic and peroxide-induced coupling of aqueous thiols - 1. Kinetic results and engineering significance' cited in the application see page 3130 - page 3133 ---	1
A	US,A,4 721 813 (H.W. MARK et al.) 26 January 1988 see example 1 ---	1
A	GB,A,787 914 (STANDARD OIL) 18 December 1957 see page 1; examples -----	1

* Special categories of cited documents :[10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
25 MAY 1993	-8. 06. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	RUSSELL F. ENGLISH

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

CA 9300055
SA 69983

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4721813	26-01-88	None	
GB-A-787914		None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82